Adsorption of eosin Y dye on Iraqi clay

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الخلاصة

تم قياس امتزاز صبغة الايوسين الذائب في الماء على الطين العراقي باستخدام كمية المادة الممتزة , حرارة الامتزاز و pH المحلول , لقد وجد ان ايزوثيرم الامتزاز مطابق الى معادلات Feundlich and Dubinin – Radushkevich . ان الامتزاز هو عملية فيزيائية باعثة للحرارة بطبيعتها مع التغير بالانثالبي عند kJ/mol (-11.87) و التغير بالطاقة الحرة عند kJ/mol (0.8-2.05) بتركيز 13.2 ppm .

ان قيم التغير بالانتروبي اظهرت بان عملية الامتزاز متوافقة مع الزيادة في عدم الانتظام و درجات الحرية عند تداخل صلب – محلول بسبب حركية جزيئات الماء و صبغة الايوسين حول سطح الجسم الماز . ان قيم pH المثلى لصبغة الايوسين المزالة كانت 3,7,11 وان امتزاز صبغة الايوسين على الطين العراقي يقل عند زيادة pH المحلول .

ان النسبة المئوية لصبغة الايوسين المزالة كانت % 42-25 عند مدى التراكيز المستخدمة في البحث وعند pH المساوي الى 3

Abstract

The adsorption characteristics of eosin Y dye dissolved in water on Iraqi clay has been measured in terms of the amount adsorbed, the heat of adsorption and PH of solution.

The adsoption isotherm of eosin was found to conform to the Feundlich and Dubinin – Radushkevich equations.

The adsoption process was exothermic and physisorption in nature with an enthalpy change ΔH of (-11.87)kJ/mol and ΔG (0.8-2.05) kJ/mol at initial con. = 13.2 ppm.

ΔS values showed that the process is accompanied by increase in disorder and randomness at the solid- solution interface due to the reorientation of water molecules and eosin around the adsorbent surface.

The optimum PH value for eosin Y removal was found to be 3,7,11. The dye was adsorbed on Iraqi clay decrease with increasing the PH of the solution . The eosin Y dye was removed by (25% - 42%) along the whole range of initial concentration at PH equal 3.

Introduction

Environmental pollution is often caused in municipal waste-waters containing organic compounds and in the purification of water. Adsorption is a physiochemical process which offers great potential as a mean of producing quality effluent (1)

The scanning tunneling microscopy (STM) and cyclic voltammetry have been employed to investigate the adsorption of eosin molecules on Au(111) in aqueous $HClO_4$ solution. The eosin molecules are found to formed a highly ordered adlayer on the well-defined Au (111) surface. A dimeric structure of eosin molecules is clearly resolved in high-resolution STM image .based on the STM observation and theoretical calibration ,a structural model is tentatively proposed (2).

The performance of activated carbon has been investigated for the adsorption of eosin dye dissolved in water. Eosin is anionic in nature and highly toxic. The effects of initial dye concentration, contact time , PH and temperature on adsorption of eosin by affixed amount of activated carbon (1.0 g/L) have been studied in batch and column mode . The equilibrium data are successfully fitted to Freundlich adsorption isotherm (3).

The previously study dealt with the adsorption of eosin Y, as a model anionic dye, from aqueous solution using chitosan and tripolyphosphate. The results showed that adsorption of eosin Y on chitosan nanoparticles was affected by contact time, eosin Y concentration, PH and temperature. Experimental data followed Langmuir isotherm model and the adsorption capacity was found to be 3.333 g/g [4].

The aim of this work is to assess the ability of Iraqi clay to adsorb eosin Y dye from aqueous solution. This studied includes the influence of temperature, dye concentration and PH of solution.

Experimental

The Iraqi clay used for the majority of these studies (obtained from river in Baghdad) prepared by mechanical grinding and sieving to obtain a relatively narrow rang of particles passing a no.500 µm. After sieving Iraqi clay was washed with acidic solution then was washed with distilled water to removed dust and fines (impurities compounds), and dried to constant weight at 100 ^{o}C . The clay was supplied from the general company of Gedogical survey and mining Iraq ,the chemical analysis of clay mentioned in table (1) .

Table (1) : The chemical analysis of clays

Clay	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Loss of ignition	Total
Kaolin	54.68	30.19	1.02	1.0	10.99	97.83

The dye used was eosin orange (B.D.H Co.) ,a sample of dye was without further purification.

The adsorption isotherms have been determined by allowing eosin solution of known initial concentration to be mixed with accurately weighted a mount of Iraqi clay in a tightly closed flask at a certain temperature and PH. The amount of Iraqi clay in the slurry has been 0.2 gm/10 ml solution. A constant mixing at a constant temperature and PH was achieved using a shaker water bath.

The Iraqi clay–solution have been then equilibrated for two hours , clay suspensions have been then filtered and the supernatant solution was subjected to analysis using ultra violet –visible technique at (516)nm , the same experiment was repeated at different initial concentration , temperatures and PH.

Results and discussion

The eosin adsorbed per unit weight of an adsorbent, q_e was calculated using the following equation [5]:

$$q_e = \frac{V_{sol}(C_o - C_e)}{m} \quad \ldots\ldots\ldots\ldots.. (1)$$

Where, C_o is the initial concentration of eosin (ppm), C_e is the residual concentration of eosin in solution (ppm), m is the mass of clay (gm) and V is the volume of eosin solution in L.

The results concerning eosin adsorption for clay are presented in figure (1) at (294K) and PH's (3, 7 and 11).

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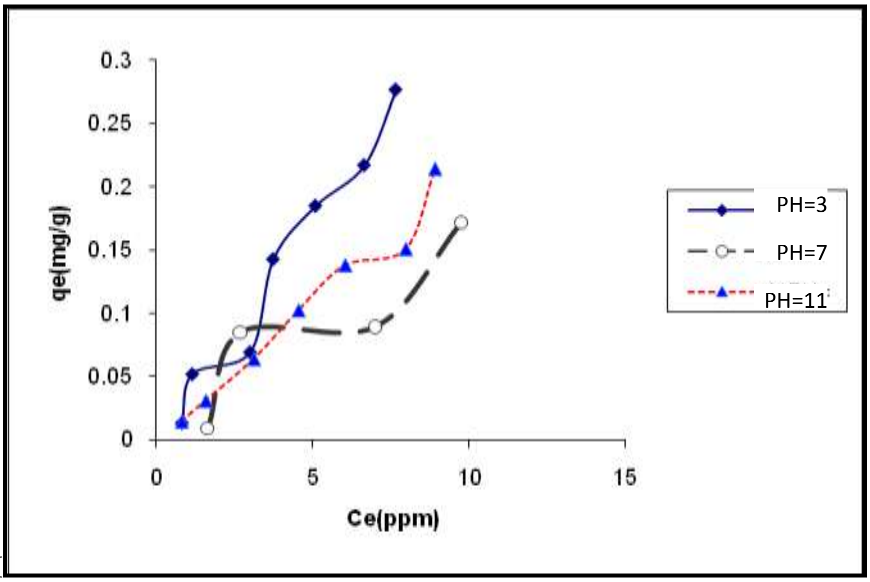


Figure (1) : Adsorption isotherm of eosin on Iraqi clay at different PHs and at 294K

It is obvious from figure (1) that the adsorption isotherms of eosin on clay are s-type according to Giles classification [6] .

In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorption and the plateau signifies the mono layer formation [7].

The initial curvature indicates that a large amount of eosin is adsorbed at a lower concentration as more active sites of clay are available, as the concentration increases , it becomes difficult for eosin molecule to find vacant sites , and so monolayer formation occurs [8].

A clay surface is heterogeneous and this feature could be attributed by the different properties of the an saturated adsorption sites with lead to different characters of these sites.

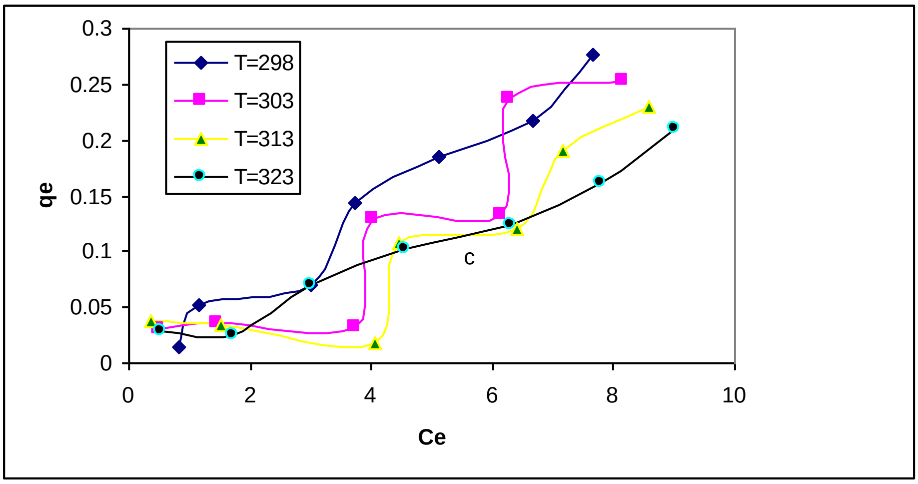
The types of system which give this curve do in fact fulfill these conditions. Thus they have one of the following characteristics:

(i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end –on ,they suffer little solvent competition .

Examples of (ii) are (a) systems with highly polar solute and adsorbent , and a non polar solvent ;and (b) systems with mono functional ionic substances with very strong intermolecular attraction .it is possible that in the system (c)cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions [9].

Effect of temperature:

The result of adsorption capacity carried out at temperatures above room temperature are shown in fig (2)



Figure(2): Adsorption of eosin on clay at different temperature and PH =3

The initial rate of adsorption is increased by an increase in temperature ,however the adsorption capacity is decreased with temperature increases the escaping tendency of molecules from the interface , and there by diminishes the extent of adsorption , a decrease in the initial rates of dye adsorption from reduces the time required to attain equilibrium [(1)].

The Gibbs-Helmholtz equation allows the calibration of ΔH°, assuming that it is independent of T:

$$\ln K_o = -\frac{\Delta H^o}{RT} + cons\tan t \quad ....(2)$$

The plots of ln K^o against 1/T for given in fig(3)

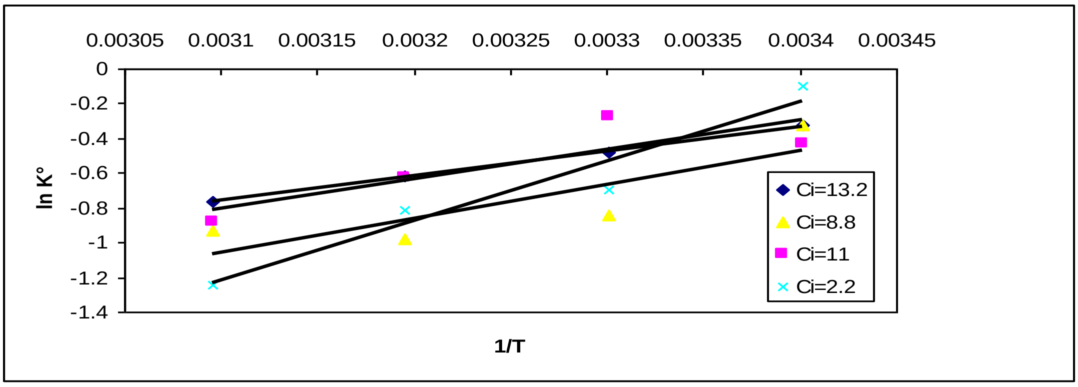


Figure (3) :Plot of Van t Hoff equation for adsorption of eosin onto clay

The ΔH° values were obtained from the slopes of these straight lines and they are compiled in table (2)

Table (2) : The thermodynamic parameters for the adsorption eosin on the clay

C° mg/L	ΔH° kJ/mol	ΔS° J/mol.K	ΔG° kJ/mol			
			294K	303K	313K	323K
13.2	-11.87	-43.1	0.80437	1.19236	1.62346	2.05455
11	-13.955	-49.9	0.725513	1.17492	1.67426	2.1736
8.8	-16.075	-58.6	1.153036	1.68043	2.26642	2.85241
2.2	-28.676	-99.1	0.448	1.33976	2.33037	3.321

ΔG° can be calculated from K values and their temperature dependence by means of equation[10]:

$$\Delta G = -RT \ln \frac{Q_e}{Ce} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Further evidence that intraparticle diffusion plays an important role in the rate-determining step in the adsorption of Eosin on Iraqi clay is confirmed by temperature dependence of the rate of adsorption.

The adsorbed amount decreased with increasing temperature. This means that the adsorption process is exothermic.

As can be seen in table (2), the isosteric heats of adsorption were (11.87-28.67)kJ/mol, in spite of using a polar molecule such as eosin.

Therefore, the adsorption of eosin is clearly due to physical adsorption[11].

On the other hand ,the changes in adsorption entropy can be calculated as translation a result of the loss of one degree of translation freedom when the adsorbate passes from the liquid phase to the standard adsorbed state .The positive and small values of Gibbs free energy (ΔG°) show that the adsorption is non-spontaneous process.

Adsorption isotherm:

Figure (4) shows adsorption isotherms of eosin on Iraqi clay in aqueous solution at 303K.

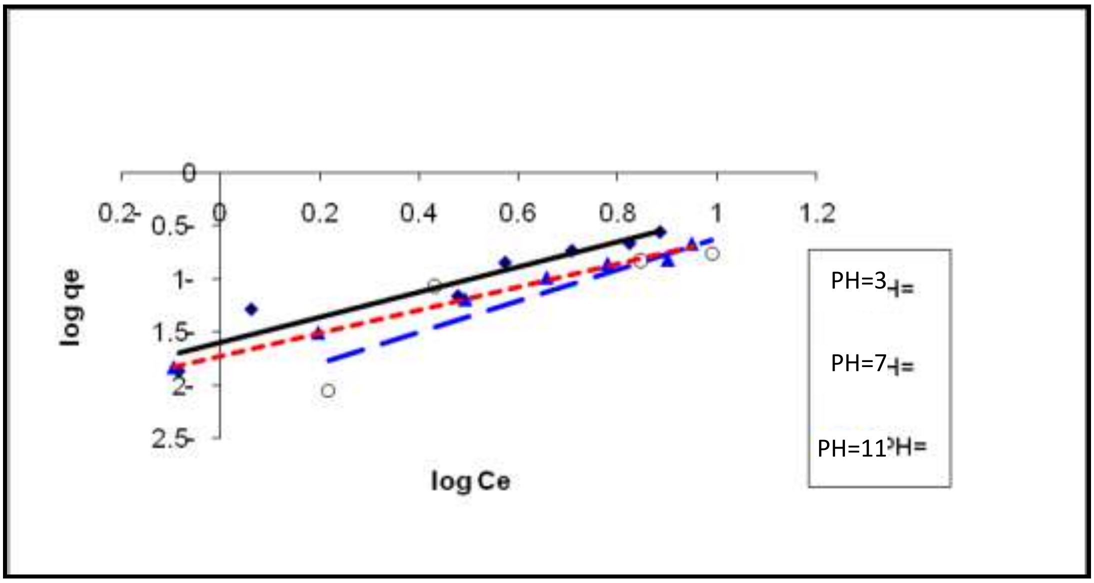


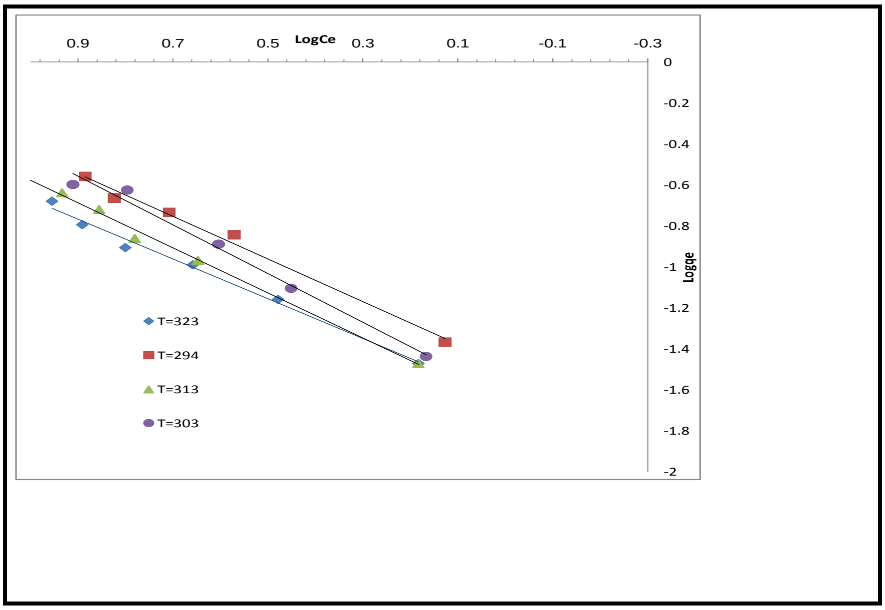
Figure (4) : Freundlish plots clay/eosin at different PH's and at 303K

As can be seen in this figure, the adsorption isotherm of eosin was found to conform with the Freundlish equation, where, the Langmuir isotherm did not give a linear plot .the Freundlish isotherm [12] have represented as:

$$\log qe = \log K_f + \frac{1}{n} \log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

A series of isotherms were determined at temperatures of 294,303,313 and 323 K respectively and the results are shown in figure (5)



Figure(5): Freundlish plots clay/eosin at different temperature and at PH= 3

The Freundlish constants are given in table (3) for a particle size range 500µm and the K_f values vary between 25.6 and 15.27.

Table (3) : Freundlish constants for adsorption of eosin at different temperatures and PH =3

Isotherm model	Isotherm parameter	Temperature			
		294K	303K	313K	323K
Freundlich	K_f	0.02566	0.02468	0.02126	0.01527
	n	0.853679	0.904241	0.9386967	0.842531
	R^2	0.9118	0.9269	0.9635	0.968

The high K_f values indicate that the saturation time for adsorption of a dye is attained quickly due to high affinity of Iraqi clay towards a dsorbate , while low K_f values indicate low adsorption rate of a dye[13]. The high value of (1/n›1) signifies that the forces which are exerted on the surface of Iraqi clay powder during a dye adsorption are strong [14].The lower temperatures indicating more favorable adsorption.

The Dubinn-Radushkevich isotherm:

The linear form of D-R isotherm equation is [15]:

$$\ln q_e = \ln Q_m - K_{D-R}\varepsilon^2 \quad \text{............... (5)}$$

Where Q_m is the theoretical monolayer saturation capacity (mg/g).

K_{D-R} is the D-R constant (mol^2/kJ^2).

ε, is the Polanyi potential and is equal to the mean energy of adsorption , E (kJ/mol)is related to K_{D-R} as [15]:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad \text{................ (6)}$$

$$E = \frac{1}{\sqrt{2K_{D-R}}} \quad \text{........................... (7)}$$

Straight lines were obtained by plotting ln qe against ε^2 for the adsorption of eosin onto Iraqi clay illustrated in fig (6) at different temperatures.

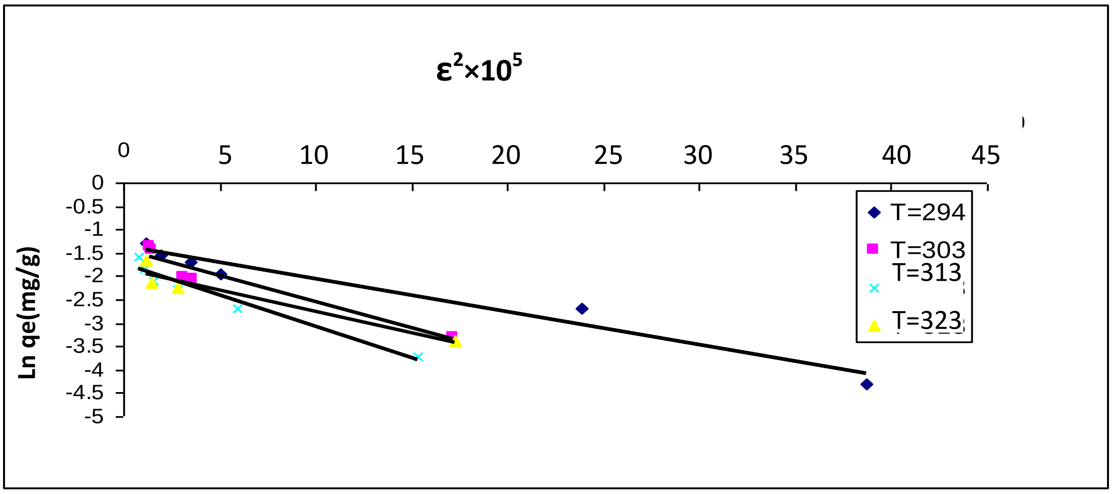


Figure (6) : D-R isotherm for the adsorption of eosin onto clay

The values of K_{D-R} and ln Q_m calculated from the slopes and intercept of D-R plots and correlation coefficients R^2, are reported in table (4).

Table (4) : D-R constants for adsorption of eosin at different temperatures and PH =3

Isothem model	Isotherm parameter	Temperature K			
		294	303	313	323
D-R	$Q_{m\ (mg/g)}$	0.25866	0.2369	0.16011	0.174575
	K_{D-R} x 10^6(mol^2/J^2)	0.7	1.0	0.9	1.0
	E (kJ/mol)	0.845	0.707	0.7454	0.707
	R^2	0.9571	0.9279	0.9228	0.9475

As can be seen in table (4) the value of adsorption energy of eosin on Iraqi clay is clearly due to physical adsorption.
The Q_m values were found to decrease in temperature, this behavior is an indication of exothermic adsorption process.

References

1. Mckay G., "*The removal of color from effluent using various adsorbents- III silica : pate processes*", *Water research* , 14, 15-20, (1980) .
2. Gui-jin su., Shu-xia yin, Li-jun wan, Jin-cai zhao., and Chun-li bai., "*Adimeric structure of eosin molecules on Au (III) surface*", *Chemical physics letters* , 370(1-2), 268-273, (2003) .
3. Purkait M.K., Das gupta S., and De S., "*Adsorption of eosin dye on activated carbon and its surfactant based desorption*", *Journal of environmental management*, 76, 350-358,(2005) .
4. Du wl., xu zr., Han xy., Xu yl and Miao zg., "*Preparation, characterization and adsorption properties of chitosan nanoparticles for eosin Y as a model anionic dye*", *J. Hazard Mater*., 153 (1-2), 152-156, (2008) .
5. Yousif M., "*Synthesis and characterization of zeolite – urea formaldehyde polymer complex and study of adsoption of some phenolic compounds from aqueous solution on its surface*", *M.Sc Thesis* , Ibn – alhaitham, College of Educational ,University of Baghdad, (2005) .

6. *Al-sharify A.N., Al-kaim A.F., Sahib R., and Kadhum A.M., "Study of the adsorption of para chloro phenol (pcp) from aqueous solution by attapulgite clay , Journal of Arab university for basic and applied sciences*, 8, 1-16, (2009) .
7. Yoshida H., Okamoto A., and Kataoka T., "*Adsorption of acid on cross – linked chitosan fibers : equilibrium", Chem. Eng. Sic*., 48, 2267-2274, (1993)
8. Gupta V.K., Moham D., and Sharmay S., "*Removal of lead from waste water using bag asse fly ash ", A sugar industry waste material, Sep. Sic. Techno.*, 33, 1331-1343, (1998) .
9. Kumar M., and Navi V.R., "*A review of chitin and chitosan applications ", React. Funct. Polym.*, 46, 2-8, (2000) .
10. Dorris G.M., "*Adsorption of hydrocarbons on thermally treated aluminosilicate", J. Colloid Interface Sic*., 82, 318, (1981) .
11. Yukihiro K., Mashiko A.B.E., and Keizo O., "*Adsorption characteristics of organic compounds dissolved in water on surface improved activated carbon fibres", Colloids and surface*, 37, 211-222, (1989) .
12. Frundlic H., *Phys. Chemi*., 57, 384, (1906) .
13. Luo x.y., Su zx., Zhang gy. and Chang xj., *Analyst* , 117, 145, (1992) .
14. Tariq S.N., Nazik J.E., and Alya A.D., "*Adsorption of copper and iron using low cost material as adsorbent", E-journal of chemistry*, 6(1), 161-168, (2009) .
15. Tariq S.N and Suhad A.Y., "*Removal of Cr (VI) from aqueous solution using modified pomegranate peel : equilibrium and kinetic studies", E-journal of chemistry*, 6(1), 129-142, (2009) .